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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE April 21, 1995	3. REPORT TYPE AND DATES COVERED Technical Report #20	
4. TITLE AND SUBTITLE Azo Polymers for Reversible Optical Storage. 8. The Effect of the Polarity of the Azobenzene Groups			5. FUNDING NUMBERS N00014-93-1-0615	
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Queen's University Kingston, Ontario K7L 3N6 Canada			8. PERFORMING ORGANIZATION REPORT NUMBER 20	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of the Naval Research 800 North Quincy Street Arlington, VA 22217-5000			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Submitted to Canadian Journal of Chemistry			19950502 058	
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14. SUBJECT TERMS azo polymers, polarity, reversible optical storage, biexponential writing and relaxation			15. NUMBER OF PAGES 21	
17. SECURITY CLASSIFICATION OF REPORT unclassified			16. PRICE CODE 0	
18. SECURITY CLASSIFICATION OF THIS PAGE unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT unclassified		20. LIMITATION OF ABSTRACT unlimited

OFFICE OF NAVAL RESEARCH

GRANT: N00014-93-1-0615

R&T CODE: 4132081

Scientific Officer: Dr. Kenneth J. Wynne

TECHNICAL REPORT NO. 20

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Submitted for publication

in

Canadian Journal of Chemistry

**Department of Chemistry
Queen's University
Kingston, On., Canada**

April 13, 1995

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Azo Polymers for Reversible Optical Storage. 8. The Effect of Polarity of the Azobenzene Groups

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Abstract

Poly[4'-[[[(2-methacryloyloxy)ethyl]ethylamino]azobenzene] (pMAEA) was prepared. Its reversible optical storage properties were studied and compared with the properties of previously reported poly [4-(2-methacryloyloxy)ethyl-azobenzene] (pMEA) and poly [4-nitrophenyl-4'-[[2-(methacryloyloxy)ethyl] ethylamino] phenyl diazene] (pDR1M). The effect of the dipole moment of the azobenzene moiety in the optical storage properties was studied by comparing the photochemically induced birefringence "writing" and "relaxation" behaviors. The writing and relaxation rates are both in the order pDR1M > pMAEA > pMEA. In addition, pDR1M, which contains donor-acceptor substituents in the azobenzene side chain, exhibits the highest saturation level of optically induced birefringence. The fraction of birefringence conserved after relaxation is lowest for pMEA, which has no donor/acceptor substituents in the azobenzene side chain, and highest for pDR1M.

INTRODUCTION

Azo polymers are attracting much attention because of their potential uses in various optical applications (1). In previous publications, we have demonstrated that stable birefringence can be optically induced in amorphous polymer thin films (2-7). The mechanism postulated for the optically induced birefringence is related to the trans-cis-trans isomerization of the azobenzene group. A series of trans-cis-trans isomerization cycles is accompanied by the movement of the azo rigid groups and eventually creates an excess of azo groups oriented perpendicular to the laser polarization direction. This dichroism produces a measurable birefringence. Circularly polarized light restores the initial disordered state of the azo groups. According to Rau (8), azo compounds can be classified into three classes: azobenzene type, aminoazobenzene type, and pseudo-stilbenes type. Azobenzenes with electron donor and electron acceptor substituents (pseudo-stilbene type) and aminoazobenzene type molecules isomerize from the cis configuration back to trans configuration very quickly at room temperature. However, the thermal cis-trans isomerization in azobenzene-type molecules is relatively slow, and it is even possible to isolate the cis isomer.

We are studying various aspects of the mechanism for the optically induced supramolecular organization and structure-properties relationship of the polymers. However, our previous studies have only focused on azo polymers with pseudo-stilbenes (2-6) and azobenzene (7) type side chain. In order to have a better understanding of the mechanism and the requirements for achieving optically induced supramolecular orientation, it is important to explore the optical properties of polymers with

aminoazobenzene type side chain. This paper presents the synthesis of an azo polymer which contains an aminoazobenzene-type group in the side chain. In addition, its optical properties are compared with two structurally similar azo polymers, pMEA (7) and pDR1M (9). The molecular structures of the three polymers compared are presented in Chart 1.

EXPERIMENTAL

The proton spectra were recorded on a Bruker AC-F 200 NMR spectrometer. UV absorption spectra were obtained from a Hewlett Packard 8452A diode array spectrophotometer. The molecular weight was obtained from a Waters Associates liquid chromatograph equipped with μ -styragel columns and a R401 differential refractometer. The glass transition temperature (T_g) was obtained with a Mettler TA 3000 thermal analysis system equipped with a TC10A TA processor and a DSC30 head.

Monomer

4'-[[[(2-Methacryloyloxy)ethyl]ethylamino] azobenzene (MAEA)

The monomer was prepared according to the synthetic scheme shown in Scheme 1. 4'-[[[(2-Methacryloyloxy)ethyl]ethylamino] azobenzene was obtained by reacting the corresponding alcohol with methacryloyl chloride. The 4'-[2-(hydroxy)ethyl]ethylamino] azobenzene was prepared by coupling the diazonium salt of aniline with 2-(N-ethylanilino)-ethanol and the procedure is as follows:

Aniline (2.4 g, 0.025 mole) was dissolved in a solution of conc. HCl (10 ml) in water (50 ml). The mixture was cooled in an ice bath until the

temperature was below 4°C. Then a solution containing sodium nitrite (1.9 g, 0.027 mole) in water (20 ml) was added slowly to the aniline solution. The mixture was allowed to stir in the ice bath for 15 minutes. The resultant solution, which contained the diazonium salt, was added to a solution of 2-(N-ethylanilino)-ethanol (4.2 g, 0.025 mole) in glacial acetic acid (10 ml) and water (20 ml). The mixture was stirred for 5 minutes in the ice bath and aqueous sodium carbonate solution was added to adjust the pH to ~6. The solid was filtered and air dried. The solid was recrystallized from ethanol/water mixture (3/2 by volume). Yield 4.5 g of 4'-[2-(hydroxy)ethyl]ethylamino] azobenzene (68 per cent): m.p. 119-120°C. ^1H NMR(CDCl_3) : δ = 1.24(3H), 1.76(1H), 3.50(2H), 3.60(2H), 3.88(2H), 6.80(2H), 7.50(3H), 7.88(4H). Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{N}_3\text{O}$: C 71.35, H 7.11, N 15.60; Found: C 71.53, H 7.29, N 15.58.

A solution of 4'-[2-(hydroxy)ethyl]ethylamino] azobenzene (5.4 g, 0.020 mole) and triethylamine (3.0 ml) was dissolved in THF (80 ml). The solution was kept in an ice bath for 10 minutes. A solution of distilled methacryloyl chloride (2.3 ml, 0.022 mole) in THF (20 ml) was added slowly to the above mixture. After the addition of methacryloyl chloride, the resultant mixture was stirred at room temperature overnight. The solvent was removed by rotary evaporation and the residue was washed with a solution of sodium carbonate (1.6 g) in water (100 ml). The product was extracted with diethyl ether and the solution was washed with water and dried over anhydrous sodium sulphate. The solvent was removed by rotary evaporation and the residue was purified by column chromatography over silica gel and eluted with chloroform. Yield 5.0 g (74 per cent) of 4'-[[2-(methacryloyloxy)ethyl]ethylamino] azobenzene as a red viscous liquid. ^1H NMR(CDCl_3) : δ = 1.24(3H), 1.95(3H), 3.55(2H), 3.72(2H), 4.38(2H),

5.60(1H), 6.12(1H), 6.80(2H), 7.50(3H), 7.88(4H). Anal. Calcd for $C_{20}H_{23}N_3O_2$: C 71.19, H 6.87, N 12.45; Found: C 70.76, H 6.97, N 12.14.

Polymer

The polymerization of MAEA was carried out in dry toluene with 1% weight 2,2'-azobisisobutyronitrile (AIBN) as initiator. The monomer was allowed to polymerize under argon at 60°C for 2 days. The polymerization was stopped by pouring the reaction mixture into methanol. The polymer was redissolved in THF and precipitated again in methanol, and finally dried under vacuum. The yield was 60 % and the polymer had an weight average molecular weight of 41000 (relative to polystyrene). From the DSC, the glass transition temperature was found to be 104°C for pMAEA. The preparations of pMEA (7) and pDR1M (9) have been reported previously.

Polymer films and optical studies

The thin films of the polymers were obtained by dissolving the polymers in THF and spin-coating onto clean glass slides. The films were allowed to dry and subsequently heated above the T_g of the polymers. Relatively homogeneous thin films from 100 to 400 nm thickness were obtained by this procedure. Film thickness was determined by interferometry. The detailed procedures for the measurement of the optically induced birefringence (2-6) and thermal cis-trans isomerization rate (10) have been described previously .

RESULTS AND DISCUSSION

The UV-Vis spectra for pMAEA, pDR1M and pMEA films are shown in Figure 1. The maximum absorbances (λ_{\max}) are 410 nm, 458 nm and 324 nm for pMAEA, pDR1M and pMEA, respectively. The UV-Vis spectrum of pMEA exhibits a high intensity band in the UV region and the low intensity band in the visible region corresponds to the absorption band of the cis isomer. These bands are characteristic for "azobenzene" type in Rau's classification (8). The UV-Vis spectra of pMAEA and pDR1M exhibit high intensity bands in the visible region which is characteristic for "aminoazobenzene" and "pseudo-stibenes" types (8). In addition, the λ_{\max} of the polymers suggests that the dipole moments of trans isomers are in the order pDR1M > pMAEA > pMEA. The absorptivity for pMEA, pMAEA and pDR1M at 514 nm are $5.8 \times 10^2 \text{ cm}^{-1}$, $3.5 \times 10^3 \text{ cm}^{-1}$ and $3.6 \times 10^4 \text{ cm}^{-1}$ respectively.

For the sake of consistency, a writing laser beam with a wavelength of 514 nm (0.7 W/cm^2) was used to induce birefringence in all the polymer films. Figure 2 shows a typical sequence of inducing and erasing birefringence for pMAEA. Birefringence is induced to a saturated level by a linearly polarized laser beam, and relaxation occurs when the laser beam is turned off at 20 seconds. As the circularly polarized laser beam is turned on at 45 seconds, the induced birefringence is "erased". Both pMEA (7) and pDR1M (9) exhibit similar write-erase profiles. The saturation level of birefringence for pMEA, pMAEA and pDR1M are 0.012, 0.026 and 0.103 respectively. This result suggests that the saturation level of the birefringence follows the order of strength of the dipole moment of the azo group in the polymer. However, it has been observed that a polymer with

nitrophenylazocarbazole in the side chain (11) exhibits a saturation level of birefringence as high as 0.09, although its λ_{max} (428 nm) is quite similar to pMAEA. This suggests that not only the dipole moment of the side group but also the presence of the nitro group may be important to achieve high induced birefringence. Since the maximum obtainable birefringence should depend on the interaction between the oriented dipoles (12), the presence of a lateral dipole can stabilize the local orientational ordering induced by the polarized laser beam. In fact, the presence of terminal nitro group in liquid crystals was found to enhance the layered smectic phase (13).

The growth and relaxation of the optically induced birefringence can be quite well described by the biexponential functions [1] and [2], respectively. In fact, equations [1] and [2] were found to give good fits to the growth and relaxation of the optically induced birefringence in other polymer systems (9,11). In order to study the structural effect on the optical properties, data from the growth and relaxation of the optically induced birefringence were analyzed by equations [1] and [2] respectively. The fitting parameters obtained are summarized in Table 1.

$$y = A(1 - \exp(-k_a t)) + B(1 - \exp(-k_b t)) \quad [1]$$

$$y = C \exp(-k_c t) + D \exp(-k_d t) + E \quad [2]$$

The writing process involves an initial "fast" response mode and a "slow" response mode. The "fast" process is associated with the trans-cis-trans isomerization rates, and quantum yields, and the local mobility of the azo group. Therefore, the "fast" process is controlled by the size of the azo group, the free volume around it and the strength of the coupling interaction

between the azo group and the polymer backbone. The "slow" process should be associated with the coupling interaction between the azo group and the polymer segments and with the mobility of the polymer segments. The parameter A in Equation [1] represents the contribution of the fast growth component with rate constant k_a . The parameter B represents the contribution of the slow growth component with rate constant k_b . Similarly, the relaxation process can be described by a "fast" mode and a "slow" mode which are represented by the term " $C \exp(-k_{ct})$ " and " $D \exp(-k_{dt})$ " respectively in Equation [2]. In addition, the parameter E represents the induced birefringence conserved after relaxation.

Growth of the optically induced birefringence

Since k_a and k_b in Table 1 represent the rate constants for the "fast" and "slow" response mode, it is clear that pMEA has a slower writing response to the writing laser beam than pMAEA and pDR1M. For all three polymers, the parameter A indicates that the "fast" response mode contribution, which is related to the isomerization and reorientation of the chromophores, is the major component of the optically induced birefringence. The probability of an optical transition from trans-azobenzene to cis-azobenzene is proportional to $|\mu \cdot E|^2$, where μ is the transition dipole moment and E is the electric field of the laser beam (14). Since the optically induced birefringence is created from the trans-cis-trans isomerization and reorientation of azo moieties, it is expected that the rate of inducing birefringence will depend on the isomerization rate. For the same electric field, azo moieties with larger dipole moments would have a faster trans-cis isomerization rate and hence a faster rate of inducing

birefringence. In addition, trans-cis isomerization rates also depend on the energy absorbed by the polymer film at the irradiation wavelength. The absorptivity of pMEA films at 514 nm is much lower than that of pDR1M and pMAEA, and most of the energy is absorbed by the cis isomers. Therefore, the trans-cis isomerization rate will be much lower in pMEA than in pDR1M and pMAEA. In spite of the low absorption at 514 nm, using a laser at this wavelength can photochemically activate the cis-trans isomerization which otherwise would be very slow thermally (15) (see also Table 1). Therefore, pMEA can still give a reasonably fast response under these experimental conditions. Although the trans-cis and cis-trans isomerizations are both photochemically activated at the irradiating wavelength, a slower writing response for pMAEA compared with pDR1M is observed. This discrepancy probably comes from the fact that pDR1M has a higher absorptivity and a larger dipole moment than pMAEA. Besides the rate of isomerizations, the rate of inducing birefringence should also depend on the molecular associations among the chromophores. The molecular associations should be, in principle, more pronounced for polymers with stronger polar groups. For pDR1M, the donor-acceptor arrangement provides a large dipole and the intra-chain and inter-chain interactions among these dipoles can create a local ordering which contributes to the observed induced birefringence.

Since the slow component in the writing process is proposed to be related to the overall motion of the polymer matrix, its magnitude should be affected by molecular weight and glass transition temperature of the polymer sample. It is expected that the higher the molecular weight and glass transition temperature of a polymer, the more difficult such motions are. Among the three polymers, pMEA exhibits the lowest glass transition

temperature and highest molecular weight (Table 2). Although k_b is not solely determined by the molecular weight, it appears that the high molecular weight of pMEA could be the reason for its smallest k_b among the three polymers studied. In spite of having the highest glass transition temperature, pDR1M exhibits the largest k_b . This result suggests that the low molecular weight of pDR1M would facilitate the mobility of the polymer matrix.

Relaxation of the induced birefringence

As shown in Table 1, the relaxation rates (k_c and k_d) also follow the order pDR1M > pMAEA > pMEA. Although the thermal cis-trans isomerization is expected to be involved in the relaxation processes, the relaxation rates are much faster than the thermal cis-trans isomerization rate for pMEA [$k_i = 1.9 \times 10^{-4} \text{ s}^{-1}$] (15). Therefore, the contribution of thermal cis-trans isomerization to the relaxation processes should be insignificant for pMEA, in this case the dipole reorientation and the relaxation of the polymer segments would be the major constituents in the relaxation processes. The situation is very different for pDR1M and pMAEA, since both polymers exhibit fast thermal cis-trans isomerization rates (Table 1) which would have a significant effect on the observed relaxation rates. Besides the contribution from thermal cis-trans isomerization, one should also consider the effect of molecular associations during the dipole reorientation. The effect of molecular associations should be more pronounced for the azo group with a stronger dipole. Therefore, the effect of molecular associations might account for the difference between the relaxation rates (k_c and k_d) of pMAEA and pDR1M. Similar to the writing

process, the slow component in the relaxation process is also related to the overall mobility of the polymer matrix. As pointed out in the previous section, the overall mobility of the polymer matrix would be affected by the glass transition temperature and molecular weight of the polymer. The higher the molecular weight and glass transition temperature of a polymer, the more difficult such motions are. As shown in Table 1, pMEA, which exhibits the lowest glass transition temperature and highest molecular weight, has the smallest k_d among the three polymers. On the other hand, pDR1M, which exhibits the highest glass transition temperature and lowest molecular weight, has the largest k_d . This result agrees with the previous suggestion that the low molecular weight of pDR1M facilitate an increased mobility of the polymer matrix.

The parameter E in Eq. 2 is time independent, thus it represents the birefringence conserved in the polymer film after relaxation. It is interesting to note that the fraction of induced birefringence remaining after relaxation is different for every polymer. The fractions of birefringence remaining after relaxation are 0.67, 0.73 and 0.84 for pMEA, pMAEA and pDR1M respectively. This result agrees with the suggestion that dipolar interactions are important to stabilize the local ordering, as discussed in previous section. In addition, the fraction of birefringence remaining increases with the increase of glass transition temperature of the polymer. This observation is reasonable because the orientational ordering conserved in the polymer will depend on the difference between the operating temperature and the glass transition temperature.

CONCLUSION

The saturated levels of birefringence were found to increase with the increase of dipole moment of the azo moiety in the azo polymers. In addition, the fraction of birefringence conserved after relaxation also follows the same trend as the dipole moment and glass transition temperature. The writing and relaxation behaviors were found to be related to the dipole moment of the azo moiety, the glass transition temperature and the molecular weight of the polymer. From a practical point of view, the azo moiety with donor-acceptor arrangement (pseudo stilbene-type azobenzene) gives the best optical properties. The pseudo stilbene-type azobenzene offers the advantages of fast trans-cis-trans isomerization and strong dipolar interactions which are important for the optically induced ordering and stability.

ACKNOWLEDGMENT

Funding from the Office of Naval Research (U.S), NSERC Canada, and the Department of Defense Canada is gratefully acknowledged.

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Table 1. Parameters obtained by fitting the birefringence growth curves and decay curves to Eq. [1] and Eq. [2] respectively. Experiments were performed at room temperature.

	pMEA	pMAEA	pDR1M
$k_a (s^{-1})$	1.45 ± 0.01	3.10 ± 0.01	4.45 ± 0.02
$k_b (s^{-1})$	0.26 ± 0.01	0.54 ± 0.01	0.58 ± 0.01
$A \times (10^3)$	11.3 ± 0.1	22.3 ± 0.1	91.5 ± 0.2
$B \times (10^3)$	1.18 ± 0.07	4.20 ± 0.07	12.4 ± 0.2
$A_n^\#$	0.905	0.841	0.881
$B_n^\#$	0.095	0.159	0.119
$k_c (s^{-1})$	0.70 ± 0.01	1.68 ± 0.03	1.90 ± 0.09
$k_d (s^{-1})$	0.037 ± 0.001	0.095 ± 0.002	0.113 ± 0.004
$C \times (10^3)$	2.35 ± 0.02	3.70 ± 0.03	7.53 ± 0.18
$D \times (10^3)$	1.86 ± 0.01	3.46 ± 0.02	7.85 ± 0.08
$E \times (10^3)$	8.41 ± 0.01	19.6 ± 0.1	84.1 ± 0.1
C_n^\S	0.186	0.138	0.08
D_n^\S	0.147	0.130	0.08
E_n^\S	0.667	0.732	0.84
$\alpha (cm^{-1})^\dagger$	5.8×10^2	3.5×10^3	3.6×10^4
$k_i (s^{-1})^*$	$1.9 \times 10^{-4} \pm 3 \times 10^{-5}$	0.53 ± 0.03	0.22 ± 0.01

$A_n = A/(A+B)$; $B_n = B/(A+B)$

§ $C_n = C/(C+D+E)$; $D_n = D/(C+D+E)$; $E_n = E/(C+D+E)$

† Absorptivity at 514 nm.

* Thermal cis-trans isomerization rate.

Table 2. The weight average molecular weight (M_w), polydispersity index (M_w/M_n) and glass transition temperatures (T_g) of the polymers investigated.

Polymer	M_w	M_w/M_n	T_g (°C)
pMEA	70000	2.2	80
pMAEA	41000	2.2	104
pDR1M	9000	1.8	116

Figure Captions

Figure 1 : UV-Vis spectra of pMEA, pDR1M and pMAEA polymer films.

Figure 2 : Write-erase profile of optically induced and erased birefringence of pMAEA with laser beam at 488 nm. Time = 0 sec.: linearly polarized laser ON; time = 20 sec.: laser OFF; time = 45 sec.: circularly polarized laser ON.

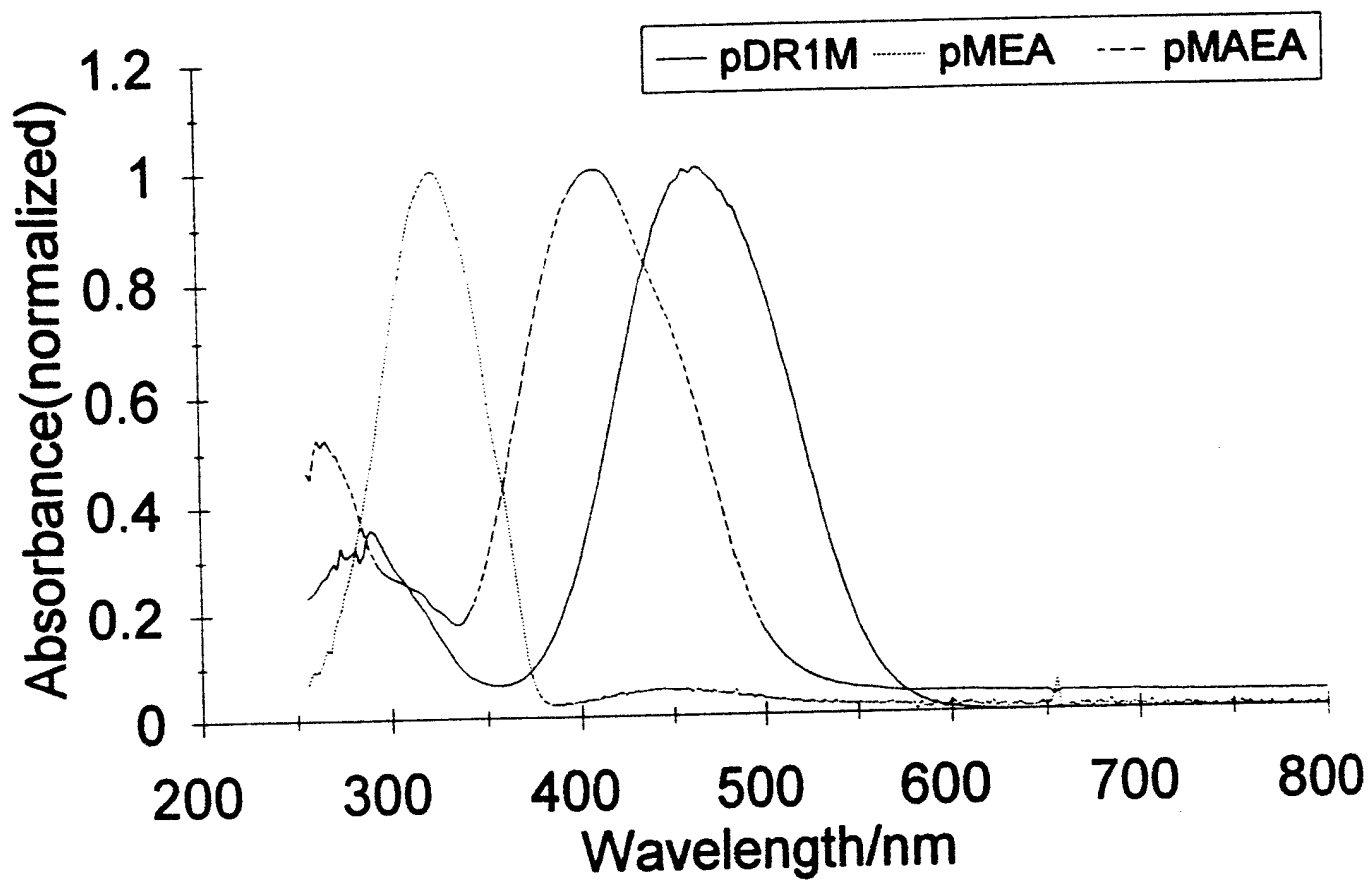


Figure 1

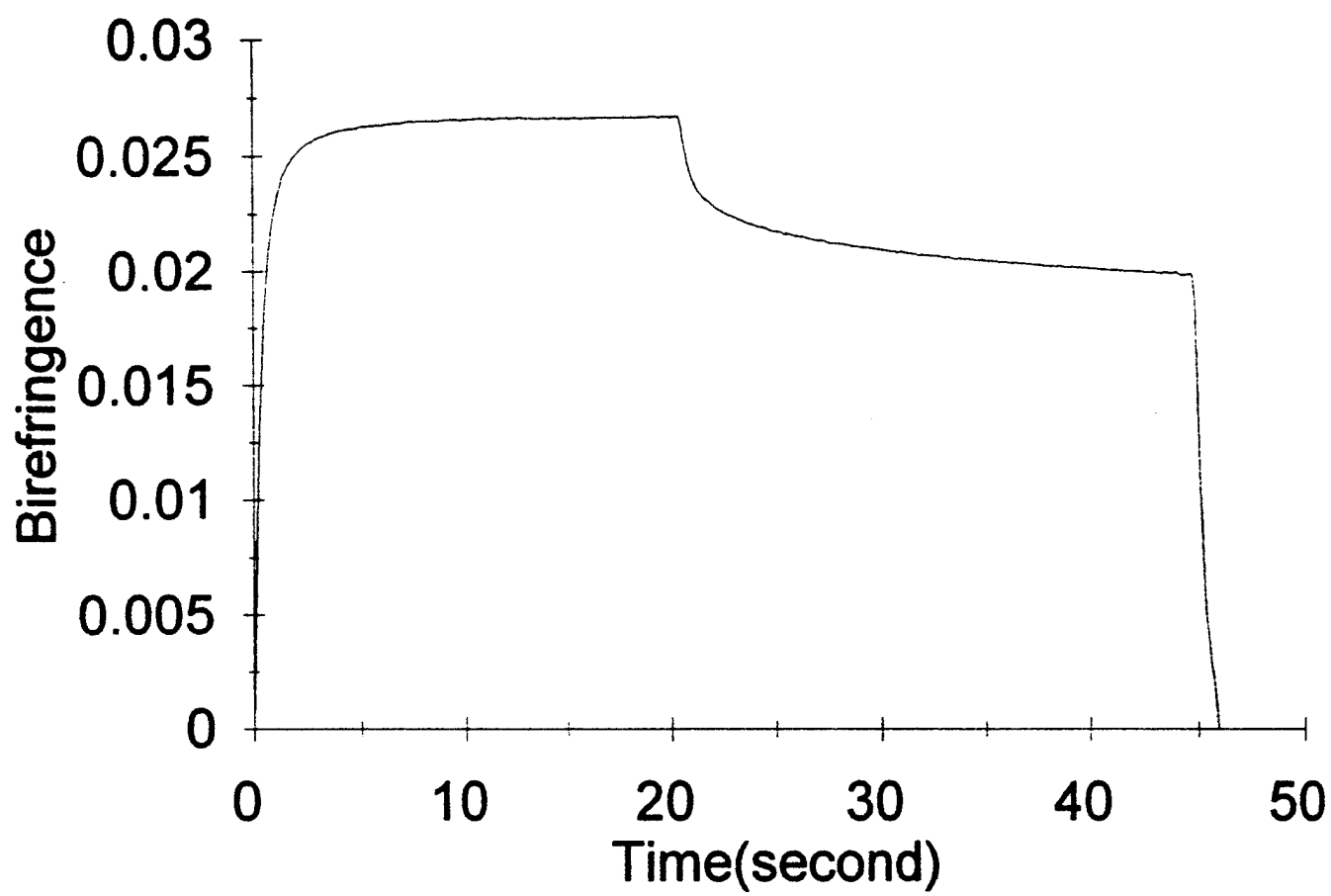
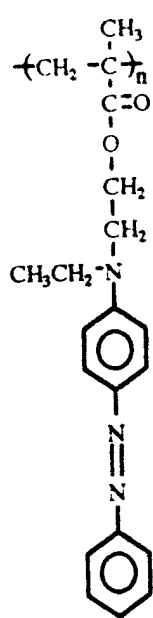
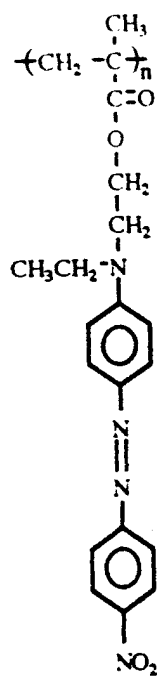


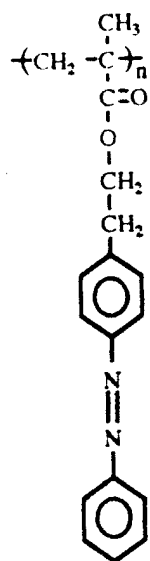
Figure 2



pMAEA

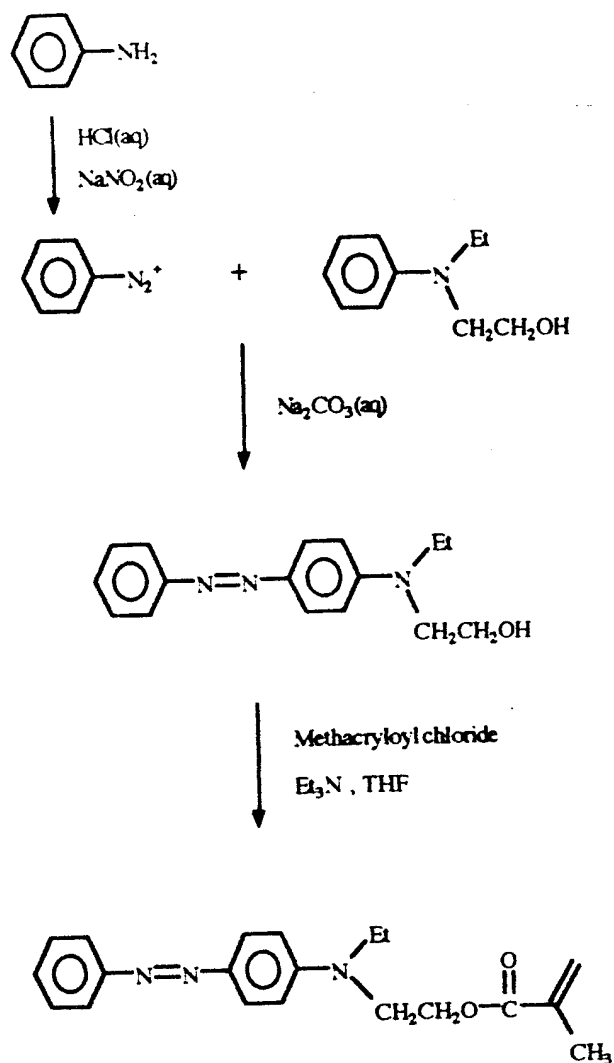


pDR1M



pMEA

Chart 1



Scheme 1